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THE PHENOMENON OF THE CRITICAL CONCENTRATION OF ACETONE  
AND A PROOF OF THE EXISTENCE OF AN INITIATING REACTION  
DURING THE OXIDATION OF PROPANE IN THE PRESENCE OF HBr

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Presented by Acad N.N. Semenov, 17 Jul 52

[Figures referred to are appended.]

In our last report [1], a new catalytic mechanism was proposed in order to explain the simple kinetic rule for the formation of acetone during the oxidation of propane in the presence of HBr (a homogeneous catalyst). This mechanism assumes the existence at the start of a rapidly flowing, self-stopping, initiating reaction, which leads to the formation of small amounts of an intermediate catalyst whose nature is thus far unknown. As a model for the initiating process, we proposed a branched chain reaction. This is the kind of reaction for which the existence of a speed limit is typical. The intermediate catalyst eventually decomposes slowly by the monomolecular rule, inducing by every act of decomposition a long chain of conversion of the initial substances into the end product of the reaction; i.e., acetone. The experimentally observed monomolecular rule for the formation of acetone follows directly from this simple model.

The present work is devoted to proving experimentally the assumption in regard to the existence of an initiating reaction at the start. While carrying out this proof, the very clear phenomenon of the critical concentration of acetone was discovered; i.e., the fact that addition of certain amounts /amounts corresponding to the critical concentration/ of acetone to the original  $C_3H_8 - O_2 - HBr$  mixture fully stops further formation of acetone.

Even in the first experiments, we noticed that the process of the formation of acetone from a mixture of  $C_3H_8 - O_2 - HBr$  ceases despite the presence of considerable amounts of the starting materials (over 50% of the starting concentrations). The catalysis mechanism proposed by us explains this phenomenon simply.

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The reaction comes to an end when the intermediate catalyst, formed in the initiating reaction, decomposes practically to completion. However, the question arises: why does not the initiating reaction start again, if there are enough initial materials present? Moreover, direct experiments with quantities of starting materials and catalyst that remain at the moment the formation of acetone ceases again demonstrate the formation of acetone.

Thus, it may be assumed that a new initiating reaction would be hindered either by those products which were formed by and stopped the preceding initiating reaction, or the end products of the principal reaction (acetone, bromo-organic compounds), or all of these substances taken together.

First experiments were made under addition of acetone, which led to the discovery of an interesting fact: in a mixture of starting materials, acetone, and catalyst in ratios corresponding to the end point of the reaction, the process of acetone formation does not take place at all. The reaction for obtaining acetone is completely suppressed. Addition of acetone in amounts exceeding the critical amount leads to the result that, in the products of the reaction, there is still only the same amount of acetone, not more (as there would be if acetone formation took place) and not less (as there would be if the critical concentration were connected with some sort of chemical equilibrium in the system).

When acetone is added in amounts less than the critical, a supplementary formation of acetone takes place in the system, but on a smaller scale than in mixtures not passivated by additions of acetone. The more acetone is added to the starting mixture, the less the amount of supplementary acetone formed.

The effect of the action of acetone additions on the entire course of the reaction is illustrated in Figure 1. The fact that draws attention is that the character of the kinetic curves for the consumption of HBr and the formation of organic acids remains completely unaltered when the amount of acetone in the starting mixture is changed.

This result directly supports the conclusion made in our last report to the effect that the formation of acetone is not a process connected with the consumption of HBr and the formation of bromo-organic compounds or the formation of organic acids, but that these reactions are parallel. The character of the kinetic curves of the reaction determined on the basis of changes in pressure is interesting. Increasing the amount of acetone in the starting mixture prevents the pressure from dropping as low as it would otherwise and therefore reduces the amount of pressure increase from the minimum. In a mixture containing a critical concentration of acetone, the pressure drop corresponds almost exactly to the amount of organic acid formed (taken as propionic), so that the stage of pressure increase is not realized at all. Analysis reveals the absence of organic peroxides when the reaction is carried out in mixtures passivated by the addition of critical amounts of acetone. These data indicate that organic peroxides are formed as molecular intermediate products only when a chain reaction of acetone formation develops in the system.

It is important that the kinetic curves for the formation of acetone in mixtures to which acetone had been added (see Figure 1), as well as in mixtures without added acetone, are well described by the equation for the monomolecular reaction with the same constant but with various degrees of extent of the reaction. In other words, additions of acetone only affect the extent of the initiating reaction, and the amount of intermediate catalyst ( $I_0$ ) obtained as a result of this reaction.

At the same time, experiments with additions of acetone refute the assumption to the effect that cessation of the development of the initiating reaction is due to inhibition by acetone, since the action of acetone begins to have effect on the

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extent of the reaction only when added in considerable amounts (see Figure 1). The initiating reaction, which proceeds in good agreement with the monomolecular rule, must flow rapidly. Furthermore, good observance of the monomolecular rule over the entire course of the reaction, notwithstanding the continuous formation of acetone, attests to the lack of an effect of acetone on the process that has already developed.

The cessation of the initiating reaction also cannot be explained by the action of the bromo-organic end compounds, which, in the beginning stages of the reaction, form only in small amounts. This assumption is refuted by direct experiments, because on adding the original mixture to a partly reacted mixture, we observe a supplementary formation of acetone despite the considerable amount of bromo-organic end products present in the system at this time.

Thus, it may be assumed that the initiating reaction is stopped by some of its own end products.

In regard to the occurrence of a critical concentration of acetone, this is a special phenomenon which, as will be seen, we were successful in using to prove the feasibility of the existence of an initiating reaction. For this proof, it is necessary to compare the action of acetone corresponding to the critical concentration on addition at the starting moment of the reaction ( $t = 0$ ), and when added a short time after the start of the reaction. In the first case, the reaction of acetone formation must be completely suppressed; in the second, after the lapse of the initiating reaction, additions of acetone should have no effect on the formation of acetone.

We performed a considerable number of such experiments at 200°. For purposes of illustration, we shall use data for the mixture of 40 mm  $C_3H_8$  + 40 mm  $O_2$  + 9 mm HBr, which reacts under formation of 16 mm of acetone at the end of the process. On addition of 32 mm  $CH_3COCH_3$  (the critical concentration), this same amount of acetone (32 mm) was found at the end of the reaction, i.e., the reaction forming the supplementary quantity of acetone was completely suppressed. (When a mixture of 40 mm  $C_3H_8$  + 40 mm  $O_2$  + 9 mm HBr had reacted for about 15 sec, 35-50 mm of acetone were added to the reacting mixture (this is an amount of acetone that exceeds the critical concentration). After 10 min, 15-16 mm of acetone more than were added were found in the mixture. This corresponds to the normal yield of acetone for this mixture.

In this manner, a simple and well-defined proof for the existence of an initiating reaction was obtained. At the same time, it has been proven that acetone acts on the initiating reaction (on the active centers of this reaction) but has no effect on the intermediate catalyst formed as a result of the initiating reaction.

Finally, we submit still another convincing proof for the existence of an initiating reaction at the start of the process. The experiment consists of the following: The mixture of 41 mm  $C_3H_8$  + 41 mm  $O_2$  + 17 mm HBr was allowed to react at 200° (see Figure 2, Item 1). Fifteen seconds after the start of the reaction, a supplementary amount of the initial mixture was introduced into the reaction vessel: 50 mm  $C_3H_8$  + 50 mm  $O_2$  (no HBr). With this, the yields of acetone (absolute) were increased in accordance with the kinetic curve (Figure 2, Item 3). In this way, by adding supplementary amounts of the starting materials to the system, a supplementary initiating reaction was induced. Then the experiment was repeated with only one change. On the 15th sec, before the addition of the supplementary quantity of starting materials into the vessel, 75 mm of acetone were added to the mixture (corresponding to the critical concentration in respect to the mixture which would be formed after the supplementary amounts had been added). The addition of acetone should have suppressed the supplementary initiating reaction. This phenomenon was in fact registered by us. Actually, the kinetic curve in the experiment, under addition of acetone, coincided with kinetic curve in Figure 2, Item 3.

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Thus, the assumption in regard to the existence of an initiating reaction during homogeneous catalysis with hydrogen bromide of the oxidation of propane has been convincingly demonstrated by direct experiment.

V.K. Tsyskovskiy [2] discovered similar phenomena of the concentration of catalytic action in the beginning stages of the process of oxidation for a reaction in the liquid phase, while studying oxidation of kerosene fractions in the presence of colloidal catalysts.

It should be noted that the phenomenon of critical concentrations of acetone could be utilized as a kinetic method for studying the kinetics of the initiating reaction and the properties of the intermediate catalyst.

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[Appended figures follow.]

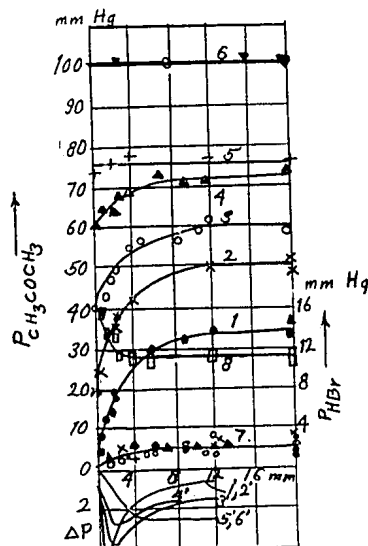


Figure 1. The appearance of the critical concentration of acetone in the oxidation of propane in the presence of HBr (glass vessel,  $d = 30$  mm). (1) kinetic curve for the formation of acetone in the mixture 80 mm Hg of  $C_3H_8 + 80$  mm  $O_2 + 17$  mm HBr; (2) the same with 20 mm  $CH_3COCH_3$  added to the original mixture; (3) the same with 40 mm  $CH_3COCH_3$  added; (4) the same with 60 mm  $CH_3COCH_3$  added; (5) the same with 75 mm  $CH_3COCH_3$  added (critical concentration); (6) the same with 100 mm  $CH_3COCH_3$  added (a concentration greater than the critical); (7) kinetic curve for the formation of acids under conditions 1-6; (1'-6') kinetic curves determined on the basis of changes in pressure for cases 1-6.

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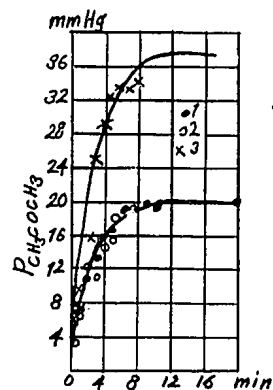


Figure 2. Experiment proving the existence of an initiating reaction leading to the formation of an intermediate catalyst. (1) kinetic curve for the formation of acetone in the mixture 41 mm  $C_3H_8$  + 41 mm  $O_2$  + 17 mm HBr; (2) the same after introduction, on the 15th sec, of 75 mm  $CH_3COCH_3$  + 50 mm  $C_3H_8$  + 50 mm  $O_2$ ; (3) the same in the mixture 41 mm  $C_3H_8$  + 41 mm  $O_2$  + 17 mm HBr after introduction on the 15th sec of 50 mm  $C_3H_8$  + 50 mm  $O_2$  (no acetone).

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